A11101 947069

NAT'L INST OF STANDARDS & TECH R.I.C.

A11101947069

/Bureau of Standards journal of research
QC1 .U52 V5;183-258;1930 C.2 NBS-PUB-C 1

DATE DUE

JUN 16 1975
7-21-87
1983

GAYLORD
PRINTED IN U.S.A.

CHANGE OF ELECTRICAL PROPERTIES OF RUBBER AND GUTTA-PERCHA DURING STORAGE UNDER WATER

By Harvey L. Curtis and Arnold H. Scott

ABSTRACT

A number of samples of rubber and gutta-percha were stored under water for about seven years and electrical measurements made on them periodically to determine the effect of aging on the resistivity, dielectric constant, and power factor. The dielectric constant was measured under three different conditions, namely, 60 cycles alternating current, pulsating direct current using 0.6 second charge with 0.1 second discharge, and pulsating direct current using the same time of charge with 1 second discharge. In all cases the dielectric constants increased with time unless failure was approached. A sample was considered to have failed when measurement of its capacitance became impracticable. The changes of the resistivity and power factor varied from sample to sample.

The approach of failure was first indicated by the resistivity. When a curve was plotted with time the sample had been under observation as abscissa and resistance of the samples as ordinates, the curves of the sample which failed showed a break or marked change in direction several months before actual failure occurred. With similar curves for power factor and direct-current dielectric constant, breaks occurred at a later time. The time interval between the break in the resistivity curve and the breaks in the other curves was a function of the rate of decrease of the resistivity. These facts indicate that the failure of a sample is the result of its decrease in resistivity. This decrease in resistivity has been ascribed to the formation of fine holes through the material. This explanation was confirmed by the microscopic examination of microtome sections of the samples which failed. These sections showed fern-like figures projecting into the rubber.

All of the samples that failed were in the form of tubes, with water electrodes both inside and outside the tubes. Some copper salts were inadvertently allowed to form inside the tubes. The catalytic action of these copper salts accelerated the aging, and probably changed its character.

CONTENTS

		Page
I.	Introduction	539
II.	Description of specimens	540
III.	Condition of test	541
IV.	Electrical measurements	541
V.	Microtome sections	542
VI.	Results	543
VII.	Discussion of results	551

I. INTRODUCTION

The dielectric constant, power factor, and resistivity of a number of samples of rubber and gutta-percha which were stored under water have been observed over a period of about seven years. During this time, measurements have been made on the average at two months intervals.[1] These measurements showed marked changes in the values of all the specimens.

The changes which have been observed are doubtless the combined effect of oxidation, water absorption, and variations in temperature.

[1] On account of the pressure of other work some of the measurements have been discontinued and others will be made at infrequent intervals. The results to date are presented in the hope that they may be of service to others who may be contemplating similar investigations.

As the specimens were always measured at room temperature, the temperature changes produced seasonal changes which can be largely eliminated by drawing smooth curves when the data is plotted with time as one coordinate. However, since water absorption increases with the amount of oxidation,[2] no attempt has been made to separate these two effects.

With some samples, the oxidation has been hastened by catalytic action of copper salts which were inadvertently present. On this account no conclusions can be drawn concerning the normal life of these rubber compounds when stored under water.

II. DESCRIPTION OF SPECIMENS

Three classes of specimens were used in this investigation. There were 3 pairs of specimens from submarine cables insulated with rubber, 11 specimens consisting of rubber tubes, and 4 specimens of gutta-percha covered wire.

The cable specimens with rubber insulation were short lengths of submarine cables which were recovered during repairs to the Alaska cable system. Two pairs of specimens were taken from the cable which had been laid from Seattle to Sitka, while the third pair probably came from the cable laid from Sitka to Valdez, Alaska. These six specimens are designated by the letter "A." The composition of the specimens taken from the Seattle-Sitka cable as reported by the manufacturing company is given in Table 1. The other pair of specimens had a slightly different composition. A complete analysis of the chemical composition of these specimens was not made. However, the ash determination showed that these specimens contained more filler than the other cables. The rubber insulation on these cable specimens was about 2.7 mm thick, and surrounded a stranded copper wire about 2.5 mm in diameter. The specimens were about 1,500 cm long.

TABLE 1

Specimen designation	Number of specimens	Form	Where obtained	Composition						
				Rubber	Paraffin	Whiting	Zinc oxide	Sulphur	Talc	Lead oxide
				Per cent	*Percent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A–1	2	Cable	Seattle - Sitka submarine cable.	40.5			5.0	1.9	44.1	8.5
A–2	2	do	do	40.5			5.0	1.9	44.1	8.5
A–3	2	do	Sitka - Valdez submarine cable.							
T–1	4	Tube	Bureau of Standards rubber laboratory.	35.8	1.4		54.1	2.1		6.6
T–2	2	do	do	40.0	1.4		48.9	2.4		7.3
T–3	1	do	do	43.8	1.7		45.3	2.5		6.7
T–4	1	do	do	43.5	1.5			2.2	47.1	5.7
T–5	1	do	do	56.8	2.2			3.2	29.1	8.7
T–6	2	do	do	40.6	1.7	16.6	32.4	2.1		6.6
G–4	1	Cable	London			[a]				
G–5	1	do	do			[a]				

[a] Gutta-percha.

[2] Lowry and Kohman: The Mechanism of the Absorption of Water by Rubber, J. Phys., Chem., 31, p. 54; 1927.

The tube specimens were made in the rubber laboratory of the National Bureau of Standards, and they are designated by the letter "T." These tubes had a wall thickness of about 1.6 mm, an inside diameter of about 8 mm and lengths varying from 1,200 to 2,800 cm. They were quite varied in composition, but were not compounded according to any logical sequence. The exact compositions are given in Table 1. In general, the time of vulcanization was such as to give maximum tensile strength, but the time of vulcanization of one set was varied to show the effect of vulcanization on life.

The gutta-percha specimens were taken from samples of gutta-percha cables obtained from an English cable company, and presumably are all alike. They are designated by the letter "G." The diameter of the wire was about 1.6 mm, the thickness of the gutta-percha surrounding it was about 1.7 mm and the length of each specimen was about 3,000 cm.

III. CONDITION OF TEST

The outer electrode for each of these specimens was the water in which it was immersed. The inner electrodes for the rubber cable specimens and the gutta-percha specimens were the wires which the insulation covered. An inner electrode for each of the tube specimens was provided by passing a copper wire through the tube and then filling the tube with water. In these cases, then, the water was on both the outside and inside of the specimen.

The specimens were coiled into coils having a diameter of about 25 cm and placed in galvanized iron containers which were filled with water. The ends of the specimens were made to extend about 15 cm above the surface of the water in the containers. Guard electrodes were provided by wrapping strips of tinfoil around the specimens about 2 cm from the ends of the specimens.

The only care given the specimens was that of replacing the water that had evaporated. The mineral content of the water probably increased slowly with time because of the use of ordinary tap water for replacing the water which was lost by evaporation. No attempt was made to regulate the temperature, but records of the temperature at the time that measurements were made were carefully kept. The temperature varied from 13° to 26° C., the average winter temperature being 17° C. and the average summer temperature 25° C.

IV. ELECTRICAL MEASUREMENTS

The capacitance was measured by two different methods, one of which used direct current and one alternating current. Two separate measurements were made using the direct-current method known as the method of mixtures,[3] the difference in the two measurements being that the cycle of voltage application was different in the two cases. In both cases, the charging time was 0.6 second. During the first 0.5 second of this charging time, the condenser was mechanically connected to the charging battery, while during the last 0.1 second the condenser was insulated. In one case, the discharge time was 0.1 second; in the other case, it was 1.0 second. In this paper the capacitance obtained by these two methods will be

[3] H. L. Curtis, Mica Condensers as Standards of Capacity, B. S. Bul., 6, p. 441; 1910.

called the "tenth-second capacitance" and the "one-second capacitance." The effective dielectric constants computed from these capacitances will be correspondingly designated.

The effective dielectric constant is computed from the capacitance measured at a stated frequency. For other than perfect condensers, the capacitance is a function of the frequency, and thus the effective dielectric constant is a function of the frequency.

The specimens were not made with sufficient exactness to permit an accurate determination of those dimensions which are required for computing the dielectric constant and resistivity of the materials. However, the same values were used in all the computations, so that the indicated changes are relatively correct. These relative changes were more important for this investigation than the absolute values.

The alternating-current capacitance and the power factor were measured at 60 cycles by means of a series inductance bridge.[4] In this paper the capacitance thus obtained will be called the "60-cycle capacitance" and the dielectric constant computed from this capacitance will be called the "60-cycle dielectric constant."

The resistance was measured by means of the direct deflection of a galvanometer.[5]

V. MICROTOME SECTIONS

Microtome sections were prepared of some of the specimens in order that they might be examined under a compound microscope. As it is impossible to cut thin sections of rubber at ordinary temperature, it was necessary to develop a special technique. The method used was a variation of the method used by Depew and Ruby.[6] It consisted of cooling the specimen to a temperature of approximately $-50°$ C., at which temperature it was sufficiently hard to permit the cutting of thin sections.

The specimen was held in the position for sectioning by freezing it to the top of a block which was clamped to the stage of the microtome. This block acted as a thermal insulator, so that the specimen could be cooled to the desired temperature without cooling the microtome. Firm bond between the specimen and the block was obtained by surrounding the specimen with water and freezing the water by means of a stream of cold air, which also served to cool the specimen.

The stream of air was cooled by means of liquid air. Air obtained from the regular compressed air line of the laboratory was passed through a drying tube to remove moisture and then carried to the bottom of a Dewar flask containing liquid air, so that it bubbled through the liquid, thus cooling to nearly $-180°$ C. Another tube leading from the stopper was directed so that the stream impinged on the specimen. The cooling of the specimen could be regulated by regulating the amount of air which passed through the Dewar flask. The arrangement can readily be understood from the diagram in Figure 1.

Since it was not feasible to measure the temperature of the specimen, the correct temperature for cutting the specimen was a matter of judgment. If the specimen was too cold, it became so hard that it

[4] F. W. Grover, Simultaneous Measurements of the Capacity and Power Factor of Condensers, B. S. Bull., 3, p. 371; 1907.
[5] H. L. Curtis and A. T. McPherson, B. S. Tech. Paper No. 299 (p. 679); 1925.
[6] Depew and Ruby, Some Microsections Cut from Vulcanized Rubber Articles, J. Ind. & Eng. Chem., 12, p. 1156; 1920.

was brittle and also injured the microtome knife. If not sufficiently cold, the specimen would give away from the knife and would not cut uniformly. As the cutting was necessarily done by a relatively warm knife, the cutting of the section tended to warm the specimen. Hence, after each cut the specimen was kept under the cold-air stream for several seconds in order to cool it to the necessary temperature for the next cutting.

The sections were permitted to reach room temperature before they were mounted in Canada balsam on a microscope slide after the method used for biological specimens. The most useful specimens had a thickness of from 5 to 10 μ. In examining the specimen a magnification of about 50 diameters gave the most useful information.

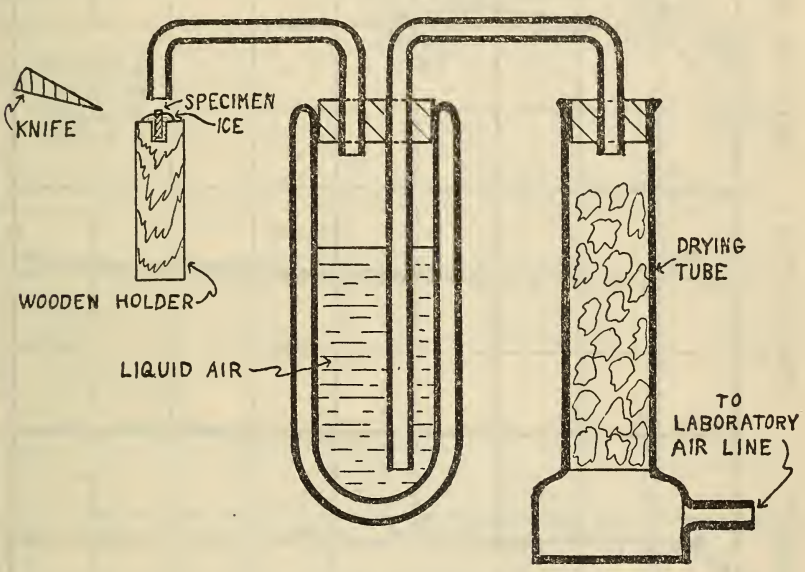

FIGURE 1.—*Diagram showing the method used to hold and cool rubber specimens for sectioning*

The specimen is cemented by ice to the top of a wooden block that is held in the clamp on the stage of a microtome. The ice is kept solid and the specimen cooled to the desired temperature by a stream of air which has been dried and passed through liquid air. The temperature of the specimen, which is regulated by the flow of air through the system, must be low enough so that the specimen will not yield under the pressure of the microtome knife and yet not be so low that the specimen is hard enough to injure the knife.

VI. RESULTS

On the basis of the results obtained from the electrical measurements, the specimens can be placed in four groups: (1) The rubber cables, (2) the tube specimens which have failed, (3) the tube specimens which have not yet failed, and (4) the gutta-percha covered wires. The complete data on only one specimen of each group are given, attention being called to any significant differences from the other samples of that group. The data are presented in the form of curves, the dielectric constants, power factor, and logarithm of the resistivity being plotted as functions of the time. The specimens which have failed are T–4, T–5, and the two specimens of T–6. The measurements were continued on these until further capacitance measurements could not be made with the equipment used, at which

time the material was considered to have failed. It might appear significant that the samples which failed contained either whiting or talc, but the specimens A–1, A–2, and A–3, not one of which has failed, also contained talc. It is impossible to compare the ageing qualities of these two types of specimens as the tube specimens were thinner than the cable specimens and their deterioration was accel-

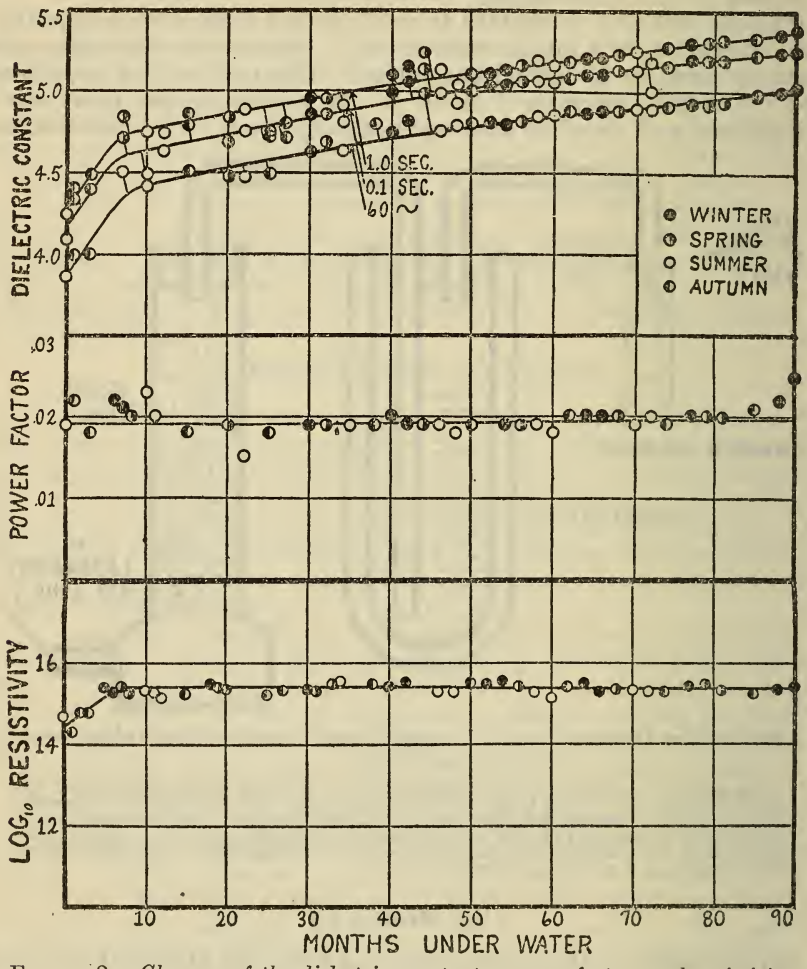

FIGURE 2.—*Changes of the dielectric constants, power factor, and resistivity of specimen A–1 with time stored under water*

This specimen was selected as typical of the group of submarine cables which did not fail during the 92 months under observation.

erated by the presence of copper salts. On the other hand, the cable specimens were in salt water at 4° C. for nearly 20 years before this investigation was started.

The results on A–1, which was selected from the group of rubber cables, are shown in Figure 2. The effective values of the dielectric constant as obtained by the methods already described are somewhat different at any one time, yet all of them increased at the rate

of about 25 per cent in 92 months. The power factor did not show any change with time. The resistivity increased during the first five months, but after that there was no permanent change. However, there were large seasonal variations, as shown by the fact that the black dots (winter observations) are nearly all above the curve, while the open circles (summer observations) are below the curve. This was probably due to the change in temperature at the different seasons.

Of the five additional cables in this group, two gave results which are somewhat different from those of A–1. Instead of remaining constant, the power factors of these increased about 46 per cent, and the resistivities decreased about 75 per cent. However, the change in effective dielectric constant corresponded to that of A–1.

The changes with time of the electrical properties of sample T–1a, which was selected as an example of the tubes that have not yet failed, are shown in Figure 3. All of the three effective dielectric constants increased more than 50 per cent in 85 months, the major part of the increase occurring in the first 30 months. Moreover, with increasing time there is a decided separation of the three curves, the one-second dielectric constant having increased appreciably more than the tenth-second dielectric constant, and this in turn more than the 60-cycle. The power factor showed continuous increase from 0.021 to 0.048, together with very pronounced seasonal variations. The resistivity decreased for the first 30 months, then became nearly stationary. This indicates a closer correlation between resistivity and effective 60-cycle dielectric constant than between resistivity and power factor.

Of the remaining specimens of this group nearly all gave results which differed from those of specimen T–1a in one way or another. In two cases of the same composition, there was no change in the slopes of the curves of the effective dielectric constants, only a steady increase, and in one other case the power factor did not change permanently. The resistivity decreased in all cases, but in three cases there was no pronounced change in slope as was the case of specimen T–1a. There is no evidence that aging in any way depends on the vulcanization. The four specimens of T–1 each had a different vulcanization and there are no marked differences in the changes of the electrical properties of these with time.

The results on specimen T–4, which was one of the group of tube specimens that failed, are shown by the curves in Figure 4. Measurements were continued on this specimen for only 62 months, at which time the deterioration had become so pronounced that no satisfactory measurements could be made. During the first 54 months the effective dielectric constants had increased nearly 100 per cent, the three curves remaining approximately the same distance apart. The resistivity and power factor were constant until failure was approached.

The first indication that the specimen was approaching failure is found in the resistivity curve. At 44 months this curve bends sharply downward making a break in the curve. Ten months later the curves of the effective one-second and tenth-second dielectric constants turn toward the effective 60-cycle dielectric constant, making breaks in these curves. Four months after these breaks there appears to be a second break in the one-second dielectric constant curve when

the values which had been decreasing begin to increase. About the time of the first break in the dielectric constant curves the power factor began to increase. However, even to the last measurement, the effective 60-cycle dielectric constant curve showed no break.

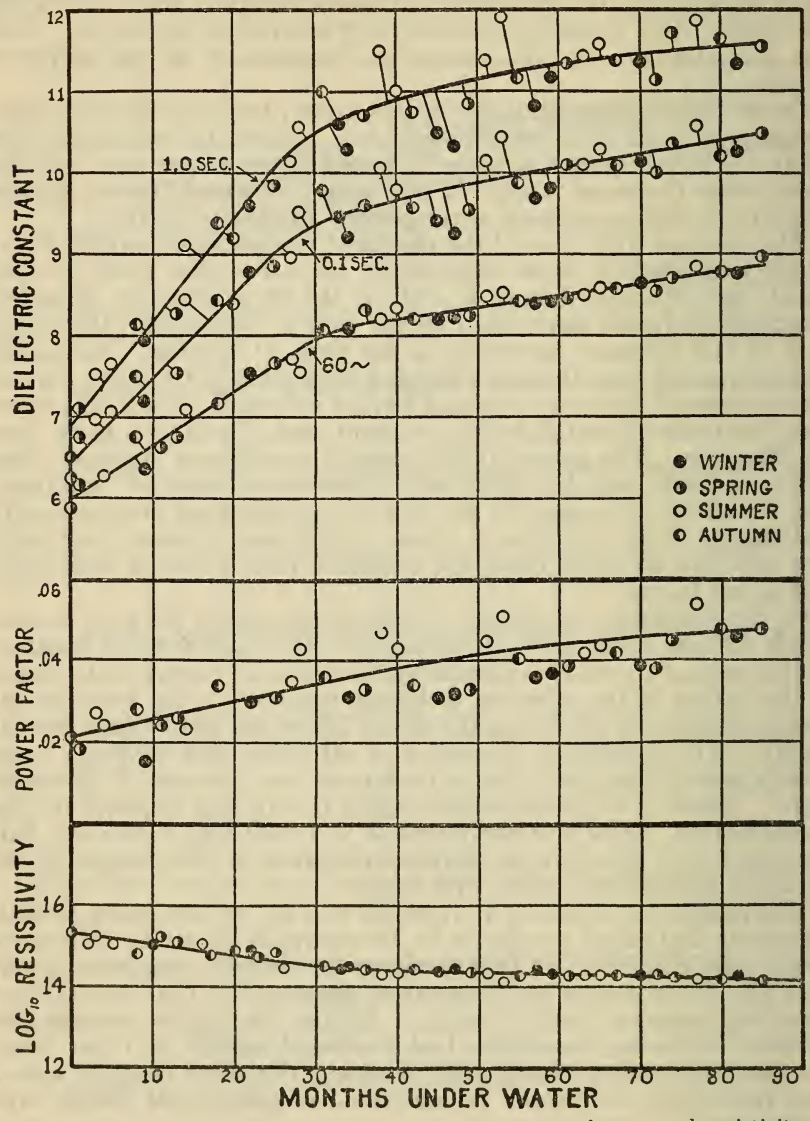

FIGURE 3.—*Changes of the dielectric constants, power factor, and resistivity of the specimen T–1a with time stored under water*

This specimen was selected as being typical of the group of rubber tubes which did not fail during the 85 months under observation.

The curves for the other three specimens of the group which failed were, in general, similar to the curves of T–4. The resistivity curves for the different specimens showed breaks at 66, 67, and 76 months. From 3 to 17 months after the breaks in resistivity curves, breaks

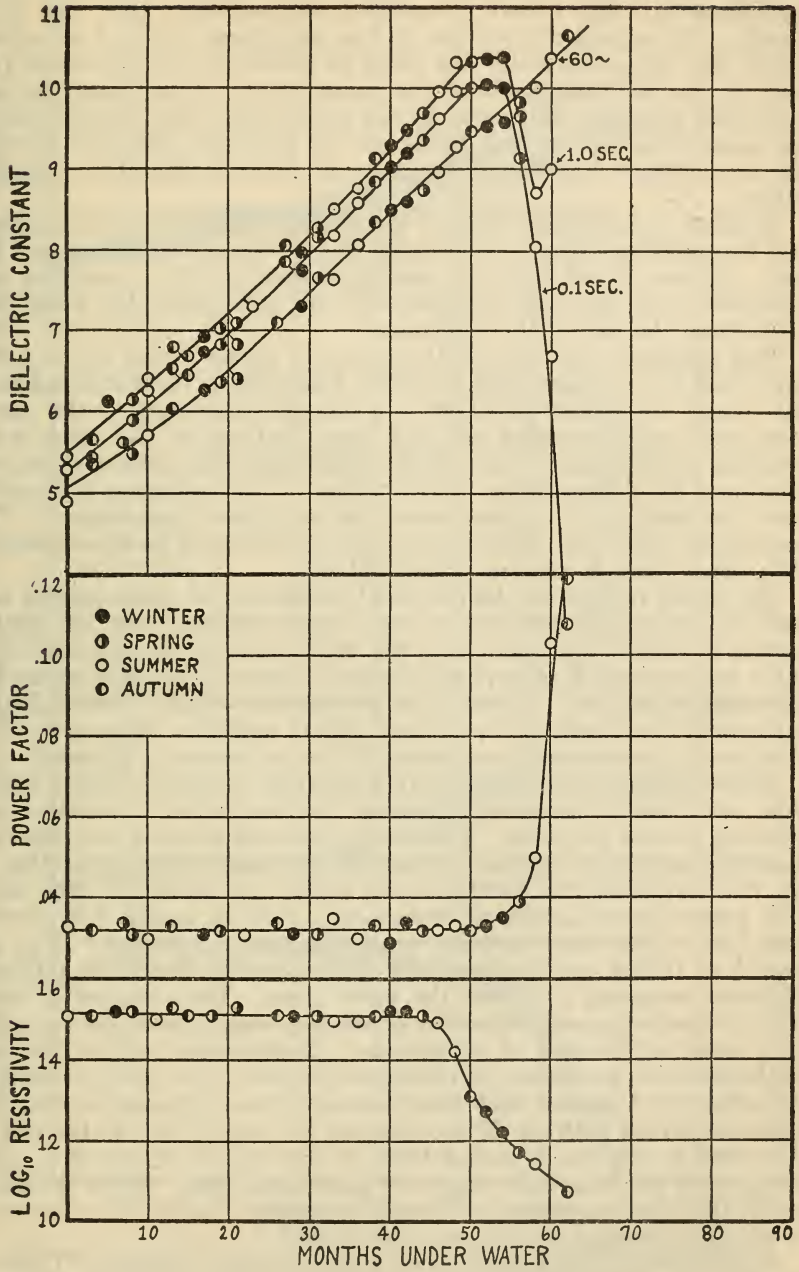

FIGURE 4.—*Changes of the dielectric constants, power factor, and resistivity of T–4 with time stored under water*

This specimen was selected as being typical of the group of rubber tubes which failed.

occurred in the one-second and tenth-second dielectric constant curves, the breaks for the two curves of any one specimen being simultaneous. At 4 and 6 months, respectively, after the first breaks, the one-second curves of two specimens showed a second break, the direction being the same as shown in the curve of T–4 (fig. 4), but the magnitude of the change being considerably larger. For every specimen the break in the power-factor curve occurred at the same time as the first break in the dielectric constant curves. For no specimen was there a break in the 60-cycle dielectric constant curve.

In order to determine whether the electrical failure was due to general deterioration or to a local fault, the specimen was tested part by part. It was found that the resistance was low for all parts of the specimen, but that the resistance of the parts near the ends was lower than the rest of the specimens.

This specimen and one of the group of tubes which did not fail were then cut to pieces and carefully examined. It was found that the copper wire which had been run through the length of the specimen was badly corroded and the inner surfaces of the tubes were greenish in color, hard and brittle, indicating that copper salts had promoted the deterioration of the rubber. This was more noticeable near the ends of the tubes where the resistance was lowest. The coating on the inner surface was more pronounced in the specimen that failed than in the one which did not.

The effect of age on the electrical properties of gutta-percha was hard to determine because of the strong tendency for the gutta-percha to crack. In most cases the crack occurred so suddenly that there was no way of observing the effect of approaching failure on the electrical properties. However, in one case the crack developed at a sufficiently slow rate so that these effects could be observed. The changes of the electrical properties of G–4 are shown in Figure 5.

Measurements were made on G–4 for only 71 months, after which time satisfactory measurements were impossible on account of the cracking of the material. During the first 60 months the effective dielectric constants increased about 44 per cent. The separation of the effective dielectric constants was small, but increased with time. The power factor increased from about 0.01 to nearly 0.04 during that time while the resistivity remained nearly constant. The approach of failure was indicated by all the curves except the 60-cycle dielectric constant at about the same time. The changes in resistivity, direct-current dielectric constants, and power factor were very rapid at the end of 60 months. There was a sudden decrease of the effective tenth-second dielectric constant. No measurement of the effective 1-second dielectric constant was obtained during the 6-month period between 60 months and 66 months but at the end of this time it was much higher than at the end of 60 months. The decrease of the resistivity was very rapid and large. As in the other cases, the effective 60-cycle dielectric constant continued to increase at about its normal rate through this period.

A summary of the results on all the specimens is given in Table 2. Only the 60-cycle dielectric constants are given. The percentage increases with time are about the same for the effective "tenth-second" and "one-second" dielectric constants as for the 60-cycle, though in every case the latter was lower than the tenth-second con-

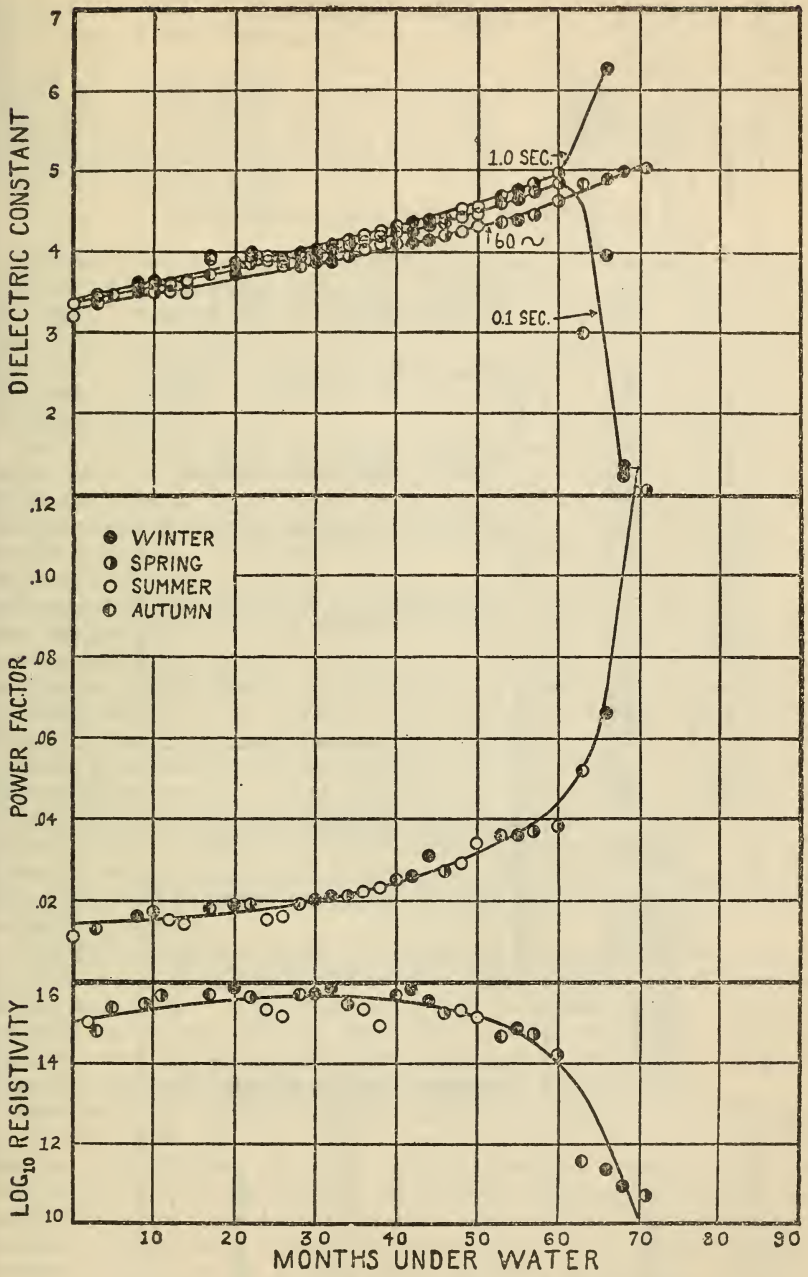

FIGURE 5.—*Curves showing the changes of the dielectric constants, power factor and resistivity of G–4 with time stored under water*

This specimen was one of the gutta-percha specimens, all of which failed.

TABLE 2

Type of specimen	Laboratory designation of specimen	Time of vulcanization at 40-pound steam pressure	Time under observation	Time to break of—		Effective 60-cycle dielectric constant		Power factor		Resistivity			
				Resistivity	Dielectric constant	Initial value	Observed increase	Initial value	Observed increase	Initial value	Value at break of—		Final value
											Resistivity	Direct current dielectric constant	
		Minutes	*Months*	*Months*	*Months*		*Per cent*		*Per cent*				
Submarine cable	A-1		92			4.0	25	0.020	20	5×10^{14}			20×10^{14}
	A-1′		92			4.0	25	.020	20	5×10^{14}			20×10^{14}
	A-2		87			4.4	7	.017	9	18×10^{14}			21×10^{14}
	A-2′		87			4.2	7	.017	9	18×10^{14}			19×10^{14}
	A-3		87			7.0	21	.026	46	15×10^{14}			5×10^{14}
	A-3′		87			6.9	23	.026	46	12×10^{14}			3×10^{14}
Tube specimens which have not failed	T-1a	15	85			5.9	53	.021	130	20×10^{14}			1.5×10^{14}
	T-1b	30	85			6.8	23	.029	60	16×10^{14}			1.0×10^{14}
	T-1c	60	85			7.0	40	.041	0	20×10^{14}			1.5×10^{14}
	T-1d	120	85			7.9	50	.047	9	17×10^{14}			0.05×10^{14}
	T-2	15	85			5.5	70	.017	100	15×10^{14}			2×10^{14}
	T-2′	15	85			6.1	41	.020	100	17×10^{14}			2.3×10^{14}
	T-3	15	81			4.7	79	.010	100	12×10^{14}			3×10^{14}
Tube specimens which failed	T-4	30	62	44	54	4.8	120	.033	4	12×10^{14}	12×10^{14}	0.57×10^{12}	5.5×10^{10}
	T-5	30	81	66	69	5.2	100	.033	12	12×10^{14}	13×10^{14}	$.12\times10^{12}$	3.7×10^{10}
	T-6	40	87	67	84	6.7	70	.026	0	11×10^{14}	1.9×10^{14}	$.18\times10^{12}$	18×10^{10}
	T-6′	40	87	76	79	5.9	68	.026	0	10×10^{14}	3×10^{14}	$.11\times10^{12}$	8.7×10^{10}
Gutta-percha	G-4		71	60	60	3.2	56	.011	250	9×10^{14}	1.6×10^{14}	$.64\times10^{12}$	5.5×10^{10}
	G-5		71	68		3.2	52	.012	250	9×10^{14}	$.1\times10^{14}$		140×10^{10}

stant, which in turn was lower than the one-second value. There was a wide variation of the percentage increase of the effective dielectric constant from specimen to specimen, but in every case there was a definite increase. There were even larger differences with regard to change of the power factor, some samples showing no appreciable permanent change with time. The resistivity showed no permanent change with time in two cases, increased in two cases, and decreased in all other cases.

VII. DISCUSSIONS OF RESULTS

The different speciments showed such a wide variation in behavior that very few general conclusions can be drawn. However, the data on every specimen under observation show that the effective 60-cycle dielectric constant increased with time as long as measurements were made. This assumes that the dimensions have remained unchanged. Whether this increase was caused by chemical changes or water absorption can not be determined from the present data.

For those specimens which failed, the approach of failure was first indicated by a marked decrease in resistivity. The observed breaks which occurred in the effective one-second and tenth-second dielectric constant curves were probably caused by the decrease in the resistance of the specimen. The capacitance of the specimen measured with one-tenth second discharge always showed a decrease when the resistance of the specimen fell below 10^{12} ohms, as shown in the next to the last column in Table 2. The capacitance measured with one-second discharge always showed a decided change when the resistance decreased to 10^{12} ohms, but this change was sometimes an increase, sometimes a decrease. In most cases, where there was an initial decrease of the one-second capacitance there was later an increase when the resistance had fallen sufficiently low. Apparently this peculiar behavior is brought about by the dielectric absorption of the specimen, but no quantitative relationship has been established. This decrease and later increase is indicated in the curve for the one-second capacitance of Figure 4, though the increase in this case is so small as to have passed unnoticed had it not been for results on other specimens.

The time interval between the breaks in the resistivity and dielectric constant curves is seen to be dependent on the rate of decrease of the resistivity. When the resistivity decreased rapidly this time interval was small. In the case of G–4 this interval was less than that between measurements and, therefore, from the curves it appears that the breaks in both sets of curves came at the same time.

The break in the power-factor curves can likewise be attributed to the decreased resistance of the specimen, and in this case the relation is quantitative. So long as the resistance remains high the power loss, due to conduction through the insulating material, is a negligible part of the total, but after the break in the power-factor curves, the loss due to the decreased resistivity accounts for the sharp increase which occurs in the power factor. A possible exception occurs when the resistivity becomes very low, but under this condition measurements of both resistance and power factor are very inaccurate.

Since all the changes in the observed curves as the specimen approached failure can be explained by the decrease in resistance, it appears that the direct measurement of the resistance is the best

method of determining the electrical failure of materials of this kind. This is emphasized by the fact that the break in the resistivity curve occurs several months in advance of the break in any other curve.

The decrease in resistance of those rubber specimens which failed is not caused by a single large hole opening through the insulation, as was shown by the measurements on one of the tube specimens, where the resistance of all parts was low. An explanation which seems to fit the facts can be made by assuming that numerous fine holes, which become filled with water, extend through or nearly through the insulation. The resistivity of water is less than one-trillionth part of that of rubber so that a very few minute holes will explain the decrease in resistance. At the same time the measured dielectric constant would not be appreciably affected by these holes, since the dielectric constant of water is never more than 30 times that of the rubber. Little is known about the power factor of water, but apparently the observed break in the power factor curve is not inconsistent with the above explanation of the cause of failure. While this explanation fits the facts, there may be others which would be equally satisfactory.

The above explanation has been confirmed by observations on microtome sections of the failed specimens. A characteristic microphotograph of a section is shown in Figure 6. Dark, fernlike figures can be seen extending into the rubber from the surface on the inside of the tube, many for at least one-third of the thickness of the rubber. While none has been observed which reaches entirely through the rubber, this is no reflection on the above theory. The chances of observing one are exceedingly small because few are required to account for the observed resistivities and the portion of the specimen represented by the sections on the slides is minute.

Since this type of deterioration occurred only where copper salts were present on the surface, it is probable that these salts have combined with the sulphur of the rubber to form cuprous sulphide, which has the dark color observed in the fernlike portions. Since copper salts were present on all samples which were observed until failure occurred, the conclusion concerning the change of electrical properties in the approach of failure may not apply to samples where such salts are not present. However, in a cable submerged in sea water, an insignificantly small penetration of water through an exceedingly small pore might start the formation of copper salts which would rapidly enlarge the hole and cause a failure of the cable.

In some cases there was considerable change of the electrical properties with the season, which probably was due to the change in temperature. This did not show up in the same property in all specimens. In the rubber cables the resistivity varied considerably with the season, while the other properties did not vary so much. In the tube specimens, the resistivity did not change much with the season, while the other properties did change. If the temperature had been controlled, better determination of the effect of time on the electrical properties would have resulted.

The authors wish to acknowledge the assistance of a number of their coworkers at the Bureau of Standards. In particular, the specimens for this investigation were made under the direction of S. Collier, and the early electrical measurements were made by Miss Johanna Busse.

Washington, February 25, 1930.

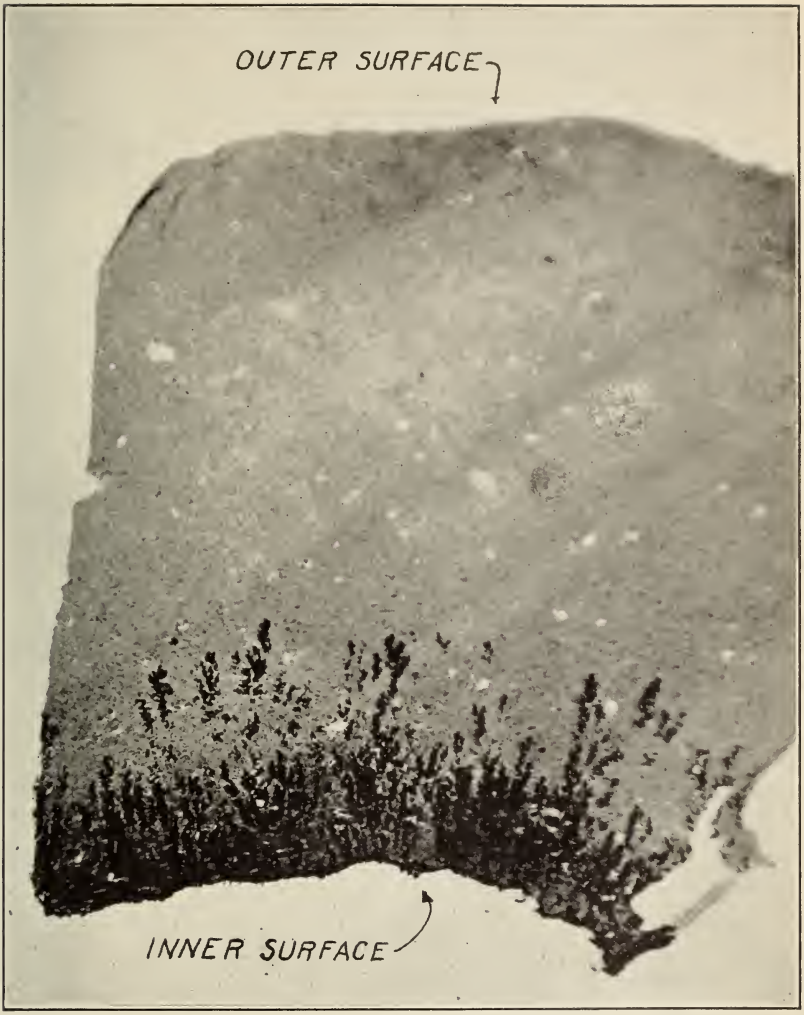

FIGURE 6.—*Microphotograph of a section of specimen T–4*

This microphotograph of a section of a tube specimen which failed shows the dark fern-like figures extending into the rubber. These figures are probably caused by the presence of cuprous sulphide.